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(6) CHROMATE-FREE METHOD OF PREPARING ALUMINUM SURFACES FOR ADHESIVE BONDING. AN ETCHANT COMPOSITION OF LOW TOXICITY.

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In a continuing effort to minimize the use of toxic and hazardous materials for the adhesive bonding of aluminum, a suitable alternative for the standard chromate-containing FPL etchant is being sought. This has resulted in the development of a chromate-free etchant of minimal toxicity, (etchant P_2) which consists of an aqueous solution of sulfuric acid and ferric sulfate. Surfaces produced with the new etchant composition when adhesively bonded result in joint strengths comparable

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to those obtained with the standard chromated etchant. Adhesively bonded 6061-T4 alloy specimens prepared with the new etchant exhibited stress durabilities superior to those prepared with the standard FPL etchant. No difficulties are expected to result from the use of the new etchant under production conditions.

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FOREWORD

The purpose of this work is to develop a new and improved non-chromated etchant of minimal toxicity. This new etchant composition must be applicable to production type conditions and produce adhesive bonds of superior durability under adverse environmental conditions.

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INTRODUCTION

Earlier work at the Feltman Research Laboratory, Picatinny Arsenal, resulted in the development of a new non-chromated etchant which is used to prepare aluminum surfaces for adhesive bonding. The use of this new etchant has resulted in the fabrication of adhesive bonded joints whose durability and strength are superior or at least equal to those fabricated with the standard FPL etchant. The composition of the new non-chromated etchant, designated "P etch", is shown in table 1. The rationale and the technique used in the formulation of the new etchant and the durability data obtained during its laboratory evaluation were first presented at the Symposium on Durability of Adhesive Bonded Structures held at ARRADCOM, Dover, NJ on October 27-29, 1976, and are contained in reference 1.

Although it has the advantage over the chromated FPL etchant of containing no chromium, P etch does contain a significant quantity of nitric acid. The presence of this acid results in the evolution of oxides of nitrogen when aluminum is being treated. These oxides of nitrogen are toxic and objectionable and must be vented. This venting results in additional heating and ventilating costs and may contribute to a drafty work site. In an effort to eliminate the necessity for venting the toxic etching fumes, a new etchant composition has been developed which does not give off any appreciable fumes and whose use results in bonds of good strength and improved durability.

DISCUSSION

Formulation of a New Etchant

In an effort to develop a non-chromated etchant composition which does not give off oxides of nitrogen when aluminum is being etched, an experimental etchant (a modification of P etch) was formulated, then evaluated. The preliminary modification was made by simply replacing all nitric acid in the P etch formula with additional sulfuric acid. This etchant was designated "etchant A" and its composition is shown in table 1. An initial evaluation of etchant A was conducted using the Rapid Universal Sensing (RUS) cell (ref. 2). Previous work has shown that data obtained using this cell can be used to screen and formulate etchants. Successful etchant compositions generate a characteristic curve when the electrode potential is plotted versus etching time. These curves are relatively smooth and attain an equilibrium potential during the etching cycle.

Table 1. Composition of etchants

Etchant	Conc sulfuric acid (g) (sg 1.84)	Ferric sulfate 75% (g)	Sodium sulfate anhydrous (g)	Nitric acid conc (ml)	Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$	Deionized water (L)	Etch temp (°C)	Cycle time (min)
A	278.0	52.0				*	-	-
B	335.0	50.0				*	-	-
C	278.0	156.0				*	-	-
D	335.0	152.0				*	-	-
E	405.0	150.0				*	-	-
F	476.0	150.0				*	-	-
P_2	370.0	150.0				*	68	16
P	37.2	54.1	69.2	218		*	66 ± 3	12
FPL	332.0				33.3	1	68 ± 3	9

*Diluted with sufficient deionized water to one liter of etchant .

When etchant A was evaluated using the RUS cell, the curves obtained were not smooth and lacked a period of stability. (During a period of stability, the electrode potential does not change with time.) When additional sulfuric acid was added to the formula, etchant B in table 1, the curve became much less stable. Figure 1 is a plot of the data obtained. Since the effect of additional sulfuric acid was detrimental, another approach was required. The concentration of ferric sulfate was increased by a factor of three and, when the etchant was tested in the cell, the curve was found to be much more stable. This formulation was designated "etchant C" (table 1). Figure 2 is a plot of the data obtained at three different etching temperatures. The curves are somewhat temperature dependent, tending to show greater stability at higher temperatures.

Figure 3 indicates that further addition of sulfuric acid to the composition causes the RUS cell curves to tend toward greater stability. The apparent anomaly with etchant E is probably due to passage through some kind of transition region. The final composition selected for evaluation (P_2 in table 1) was based on using enough sulfuric acid to insure stability while keeping the content low enough to minimize sludge formation (See Processing Characteristics, below.)

Evaluation of P_2 Etch

The new P_2 etch was evaluated for its effectiveness as a pretreatment prior to the adhesive bonding of aluminum surfaces. Simple lap joints were tensile tested to failure to determine bond strength. Wedge tests were evaluated under conditions of high temperature and humidity to determine the durability of the adhesive bond (refs. 3,4). Stress durability testing was conducted to determine the stress durability of the bonded joints.

The tensile tests were conducted at room temperature (20 $\pm$ 2°C) and at 60°C using a 2.5 cm (1 in.) wide, 1.25 cm (½ in.) lap joint made with 0.16 cm (0.063 in.) thick 6061-T6 aluminum alloy sheet. The data obtained are shown in table 2. These data show that the bonds prepared with the new etchant are essentially the same or even slightly (about 2%) stronger than those prepared with the standard FPL etchant. This indicates that the bond strength is not adversely affected by the use of the experimental P_2 etchant.

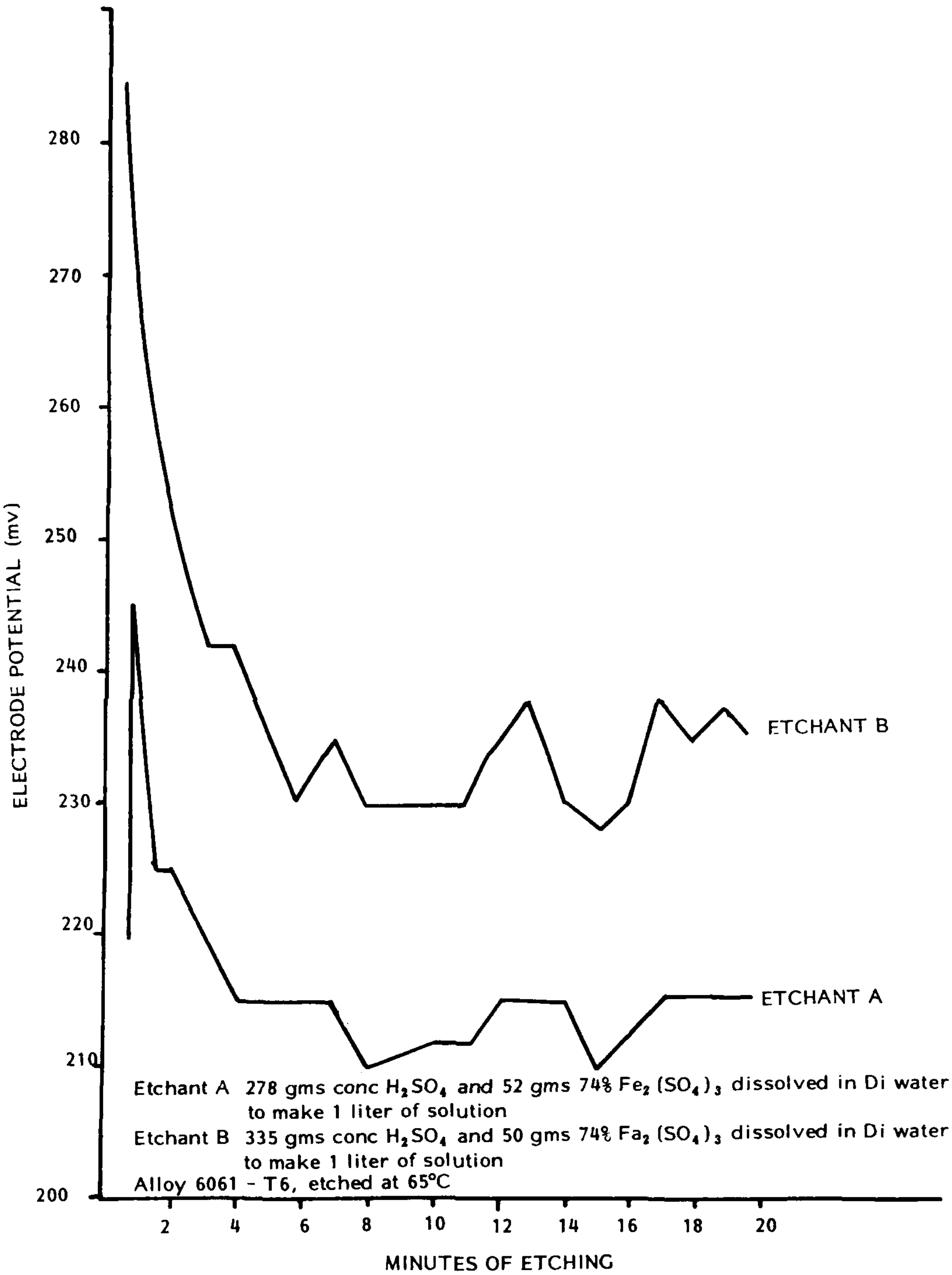

Figure 1. RUS cell curves showing effect of H_2SO_4 addition to etchant A

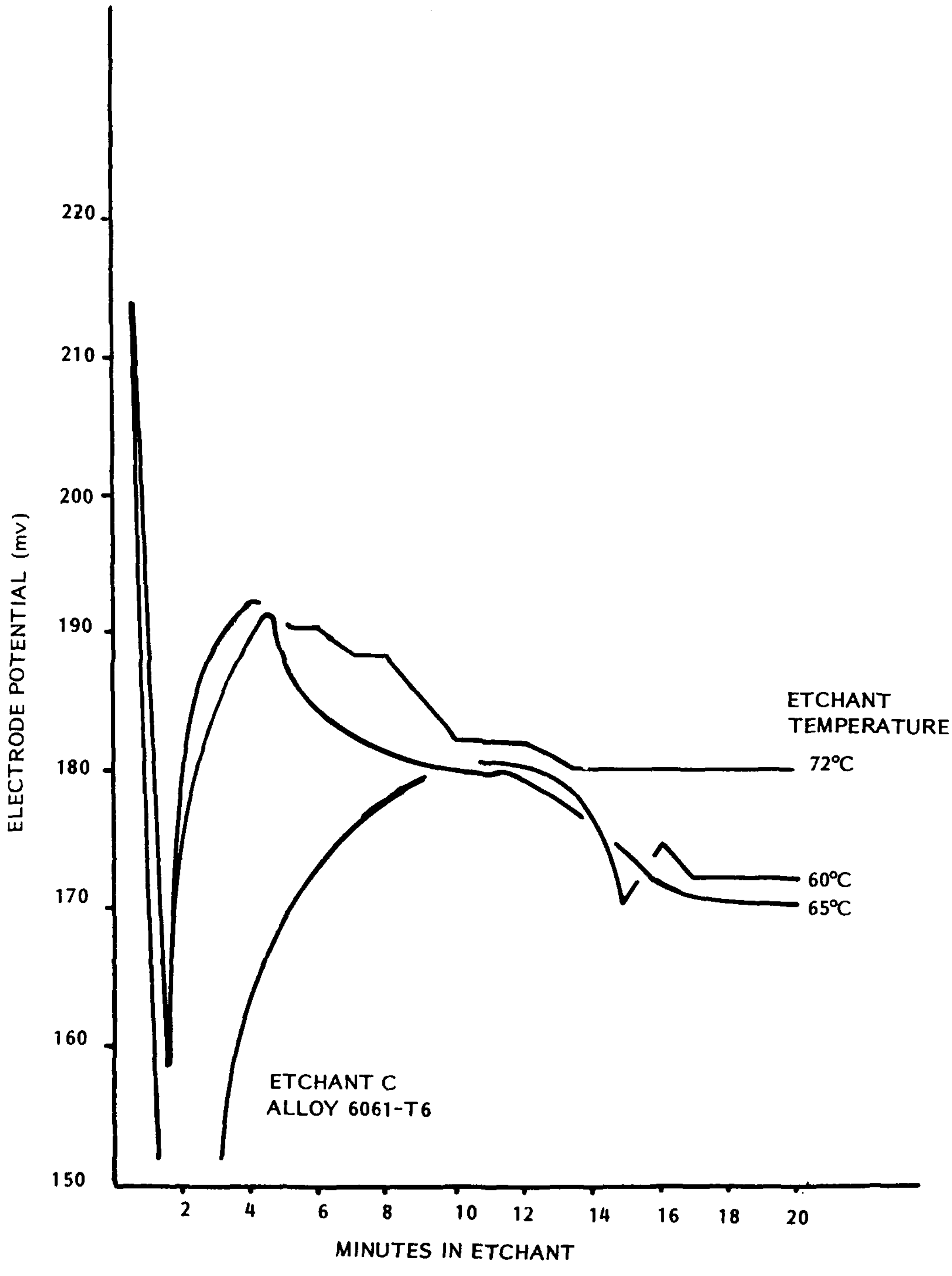

Figure 2. RUS cell curves showing the effect of $Fe_2(SO_4)_3$ addition to etchant

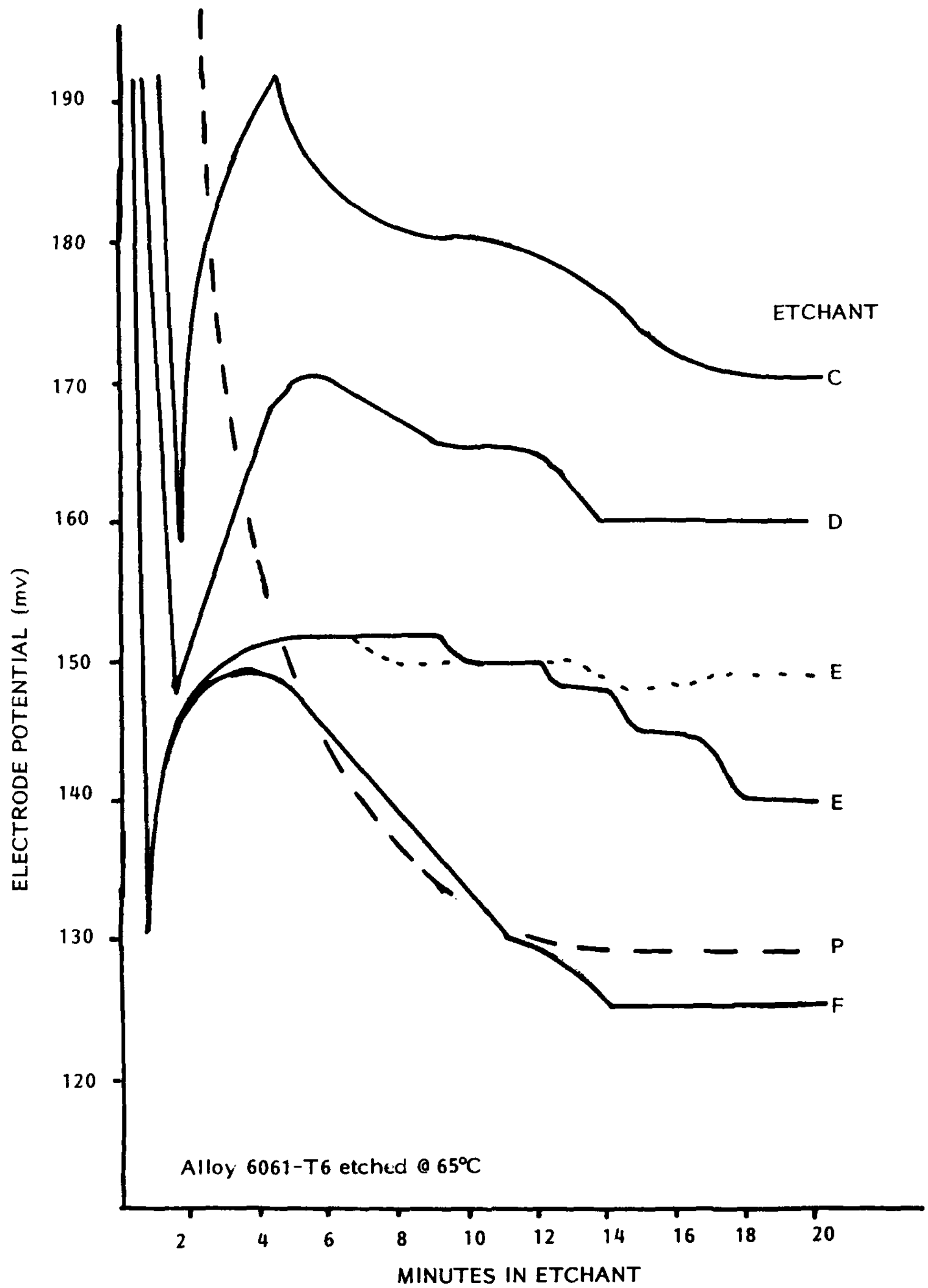

Figure 3. RUS cell curves showing the effect of sulfuric acid additions to etchant C

Table 2. Shear test results comparing two etchants on 6061-T4 alloy*

Etch	21°C Load at Break (kg)	(lb)	(MPa)	(psi)	60°C Load at Break (kg)	(lb)	(MPa)	(psi)
FPL	1165	2565	17.7	5130	670	1480	10.2	2960
FPL	1140	2515	17.3	5030	825	1820	12.5	3640
FPL	1145	2520	17.4	5040	805	1775	12.2	3550
FPL	1160	2555	17.6	5110	725	1595	11.0	3190
$\bar{x}$	1150	2540	17.5	5080	760	1670	11.5	3340
P_2	1200	2640	18.2	5280	835	1845	12.7	3690
P_2	1200	2640	18.2	5280	810	1785	12.3	3570
P_2	1190	2620	18.1	5240	815	1800	12.4	3600
P_2	1100	2420	16.7	4840	815	1795	12.4	3590
$\bar{x}$	1170	2580	17.8	5160	820	1805	12.5	3610

*Specimen configuration was the same as that used for the stress durability test.

Wedge test specimens were prepared to evaluate the durability of adhesive bonds under conditions of elevated temperature and humidity. Three sets of 6061-T4 aluminum alloy specimens were prepared using the standard FPL etchant, the P etch, and the P_2 etch. The specimens were bonded using an older type film adhesive AF-126-3. When these were tested under conditions of elevated temperature, 60°C, and condensing humidity, the specimens made with the experimental P_2 etch were found to be superior to all others. The results of this series of tests are shown in figure 4. As an additional check, four wedge-test specimens were prepared using aluminum alloy 6061-T4 for two of the specimens and 2024-T3 aluminum alloy for the other two. Specimens prepared with the standard FPL etchant were evaluated against those prepared with the experimental P_2 etch. These specimens were tested at 60°C and 100% condensing humidity. The data obtained from these tests establish that the 6061 aluminum alloy specimens prepared with the experimental P_2 etch were decidedly superior to the FPL-etched 6061 aluminum alloy specimens and comparable to the specimens made from 2024-T3 aluminum alloy. These results were unusual, since earlier specimens prepared from the 2024-T3 material were consistently superior to those prepared from the 6061-T4 alloy. The 2024 alloy wedge specimens prepared with the standard FPL etchant and the experimental P_2 etch were comparable when tested. The results obtained during this series of tests are shown in figure 5.

Stress durability tests were run as a further check of the quality of adhesive bonds prepared with the experimental P_2 etch. The stress durability test evaluates the durability of adhesive bonds under shear stress instead of under the cleavage opening mode experienced by the wedge specimens. Also, the load on the specimen is frequently much greater than that experienced by the wedge specimen. Specimens prepared from 6061-T4 aluminum alloy etched with P_2 etch and bonded were evaluated against sets of specimens prepared from both 6061-T4 and 2024-T3 etched with the standard FPL etchant and bonded. The results were similar to the wedge test results. The P_2 etched 6061-T4 alloy specimens were superior to both sets of specimens made from 6061-T4 and 2024-T3 alloys and etched with the FPL etchant. As noted above, when all other factors are equal, specimens prepared from 6061-T4 alloy do not normally exhibit stress durability results that are superior or even equal to those made from 2024-T3 alloy. The results of these tests are shown in figure 6.

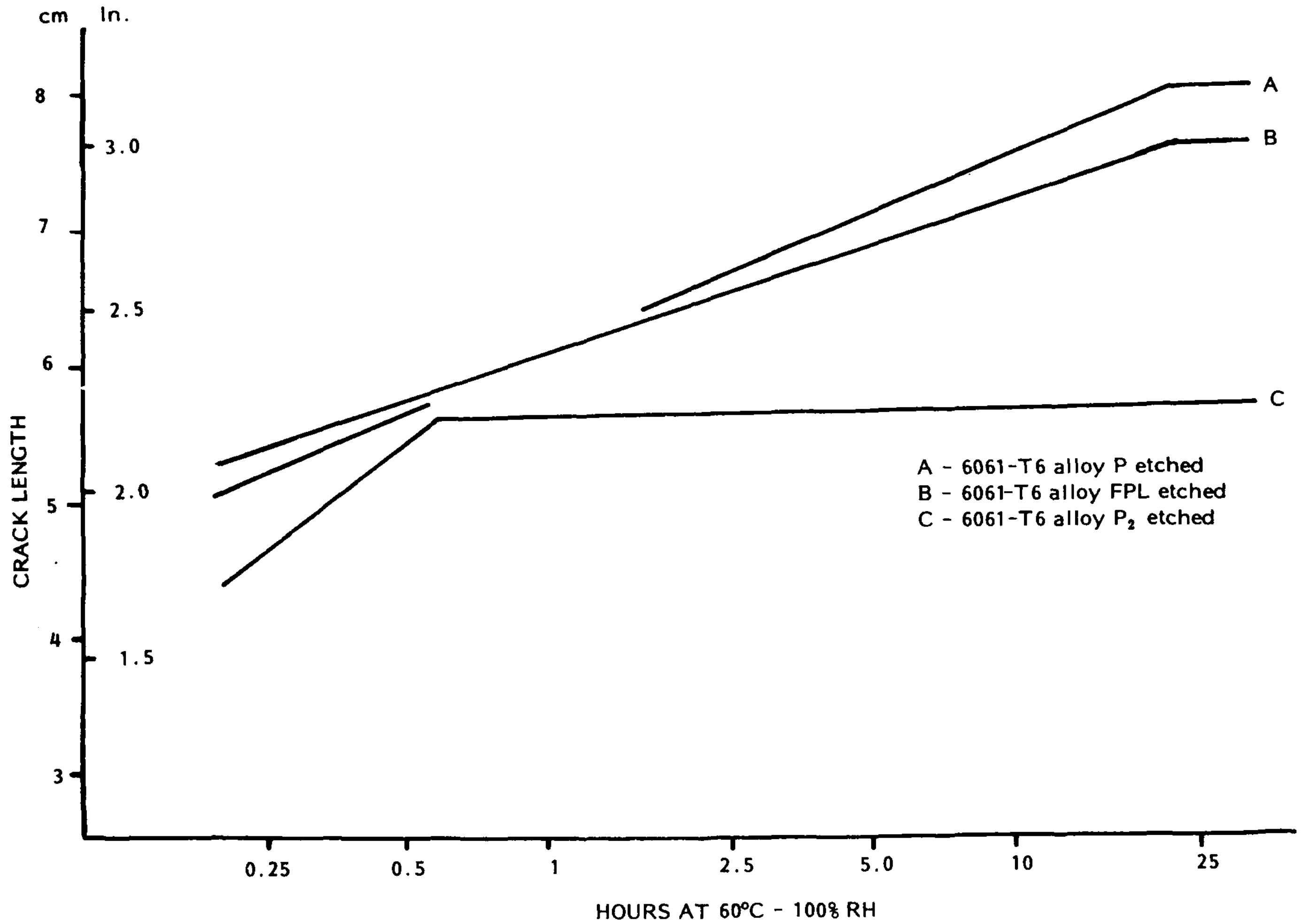

Figure 4. Wedge test results comparing durability of adhesive bonds made with three different etchants

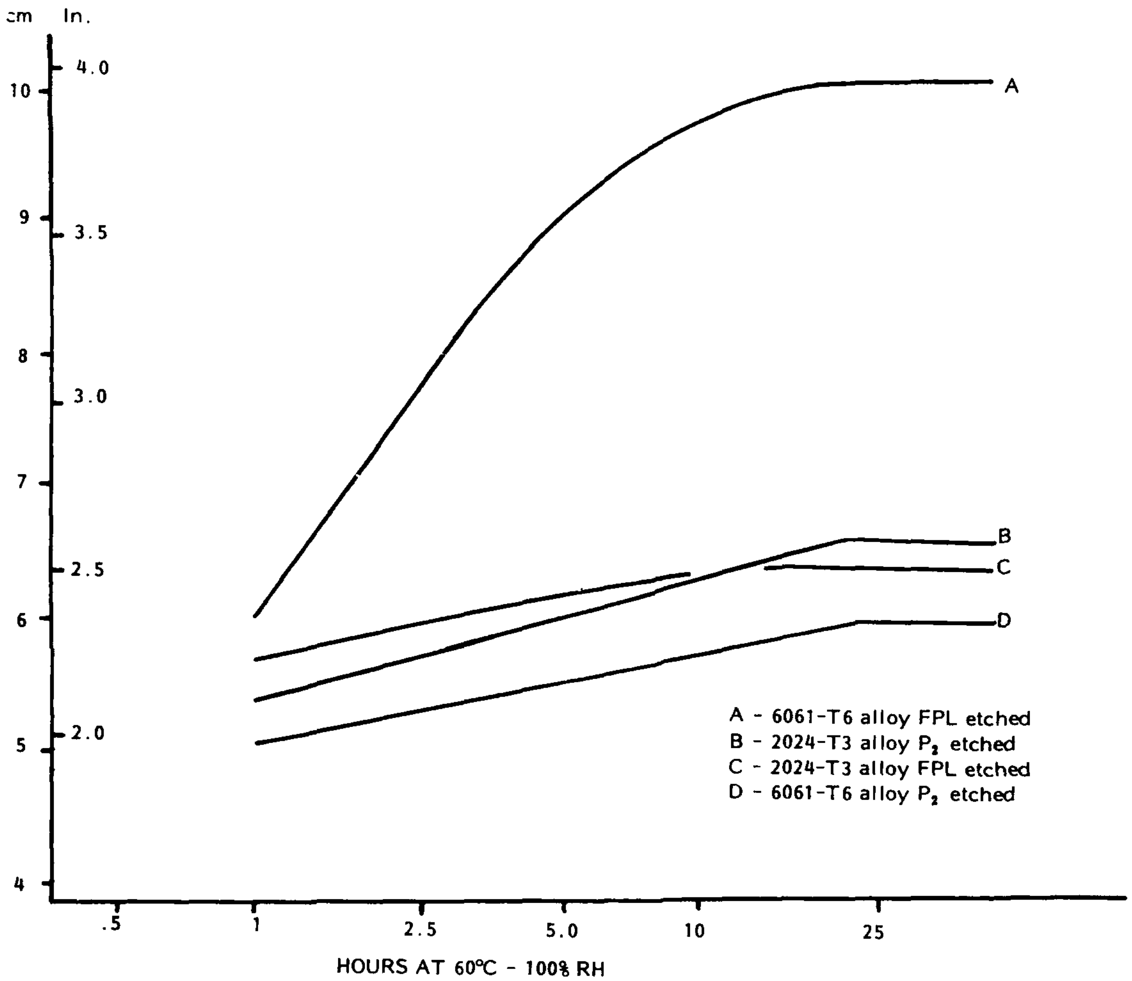

Figure 5. Wedge test results comparing durability of adhesive bonds using various alloys and etchants

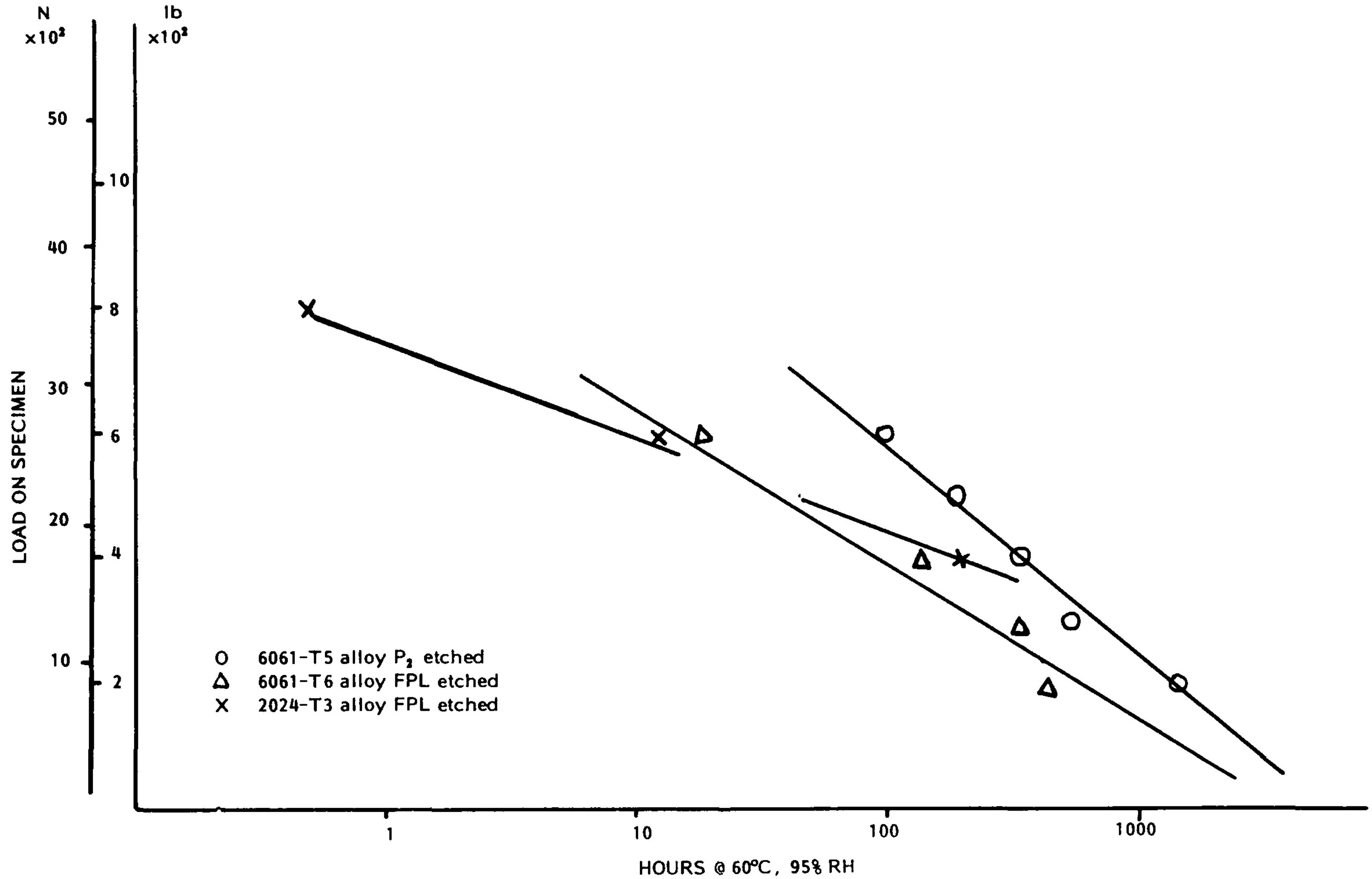

Figure 6. Stress durability test results

PROCESSING CHARACTERISTICS

The expected tank life of the P_2 etchant composition has not been estimated, but it has been noted that, upon prolonged usage, salts precipitate out of solution forming a thick layer of sludge in the bottom of the tank. This is caused by the evaporation of water from the hot etchant. A loss of as little as 10% of the tank volume due to evaporation is sufficient to cause this problem, but when the lost water is replaced, the salts go back into solution. The addition of excess sulfuric acid to the formula aggravates the problem.

The processing temperature is essentially the same as that used for the standard FPL etchant, but the normal processing time is doubled. There appears to be no serious limitation to its use under production conditions.

EXPERIMENTAL

Materials

Aluminum

Standard commercially available aluminum sheets were purchased in the required alloy temper designations and thicknesses.

Adhesive

AF 126-3 0.29 kg/m^2 (0.06 lb/ft^2) is a non-volatile thermosetting film adhesive designed for structural bonding of metals. Manufactured by the 3M Company, it is cured at 121°C in one hour at 344 kPa (50 psi).

Test Methods

Rapid Universal Sensing (RUS) Cell

The specimens, 2.5 x 10.0 x 0.16 cm (1 x 4 x 0.063 in.) strips of aluminum alloy, were carefully cleaned with acetone. They were connected to the potentiometer and immersed in the etchant. The electrical potential developed as a function of time was recorded and the curves were plotted from these data. The construction of the cell is shown in figure 7.

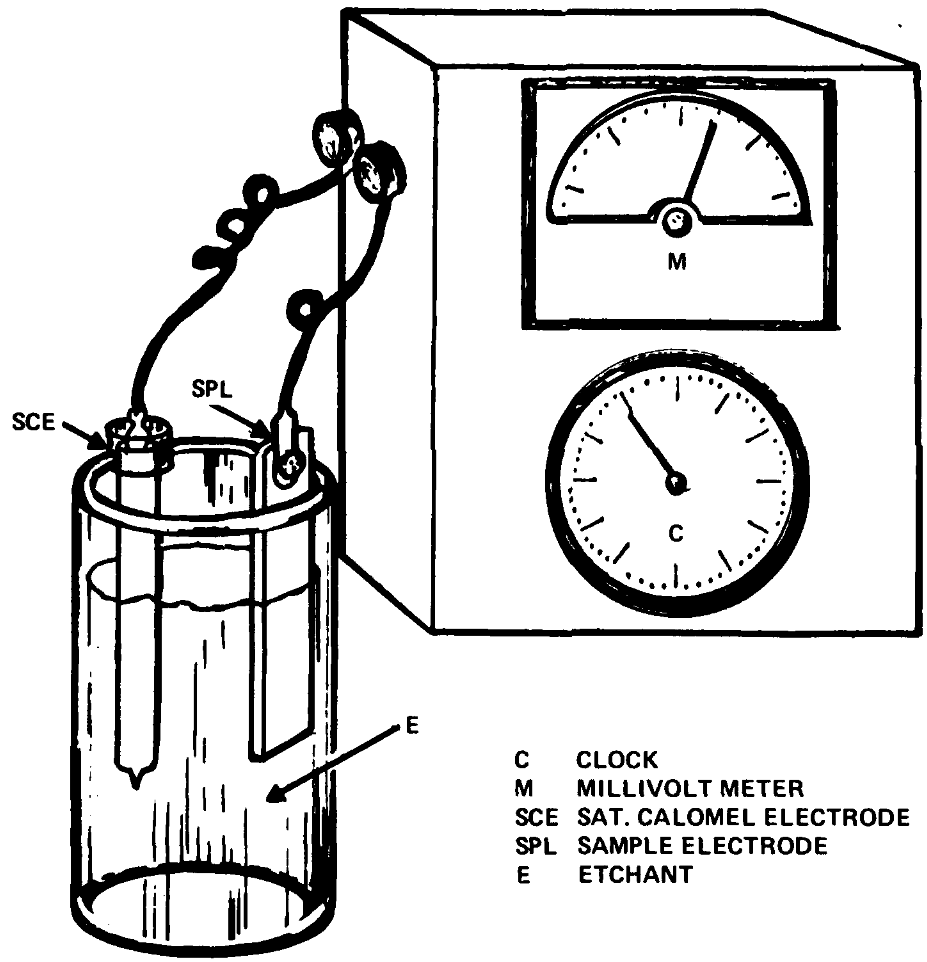

Figure 7. Rapid universal sensing cell

Wedge Test

The wedge test specimens used for this work consisted of two strips of aluminum alloy sheet 2.5 cm (1 in.) wide, 0.32 cm (0.125 in.) thick, and 20.4 cm (8 in.) long. After being cleaned with acetone, etched, rinsed, and dried, they were stacked one on top of the other with a strip of adhesive 2.5 cm (1 in.) wide by 15 cm (1.6 in.) long and a strip of teflon film 2.5 cm (1 in.) wide by 5.4 cm (2.1 in.) long by 0.1 mm (.004 in.) thick placed between them. After bonding, the teflon film was removed, creating a rectangular bonded area 2.5 cm wide by 15 cm long between the two strips of metal.

Prior to testing, a wedge consisting of a 2.5 x 1.0 x 0.32 cm (1 x 0.4 x 0.125 in.) strip of aluminum alloy was inserted into the unbonded area between the strips so that it was flush with the edges of the specimen. This wedge at no time approached closer than 4 cm (1.6 in.) to the adhesive bonded area. The stressed specimen was then placed in a test environment of 60°C and 100% condensing humidity. The growth of the crack which developed in the adhesive bond was monitored by removing the specimens from the test environment and locating the crack tip with the aid of a 40-power binocular microscope. The location of the crack was scribed on both sides of the specimen which was then returned to the test chamber for another interval of testing.

Stress Durability

Stress durability testing was conducted in accordance with the basic method described in ASTM D 2919-71, except that each fixture was equipped with a remote reading elapsed-time indicator to record the time-to-failure for each specimen. This timing device is described in reference 5.

CONCLUSIONS

1. The new non-chromated P_2 etch composition is a promising substitute for the chromated FPL etchant.

2. Aluminum alloy 6061-T4 substrates prepared with this new etchant composition have superior bond durability under adverse conditions. This suggests that the durability of adhesive bonds prepared with the less durable alloys can be upgraded, especially when clad sheet is to be used.

3. Specimens prepared with the new etchant composition have shear strengths comparable to those prepared with the standard FPL etchant.

4. No difficulties are expected to result from the use of the new etchant under production conditions.

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